

P9MOD: COKE RESISTANT TUBES/PIPES DEVELOPED BY VALLOUREC FOR REFINERY FURNACES

Olivier Hamart¹, Javier Pirón²

¹ Vallourec Tubes France

² Vallourec Research Center Germany (VRCG)

► Reasons of development of this new material?

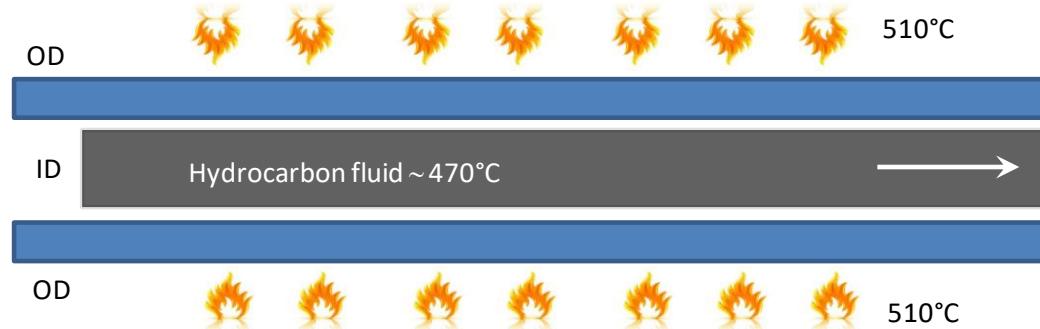
- Coking formation
 - » Coke formation is a severe problem. A progressive fouling of the internal walls of pyrolysis coil and on surface of quench exchanger takes place in service, due to presence of unsaturated species and depending on the operating conditions



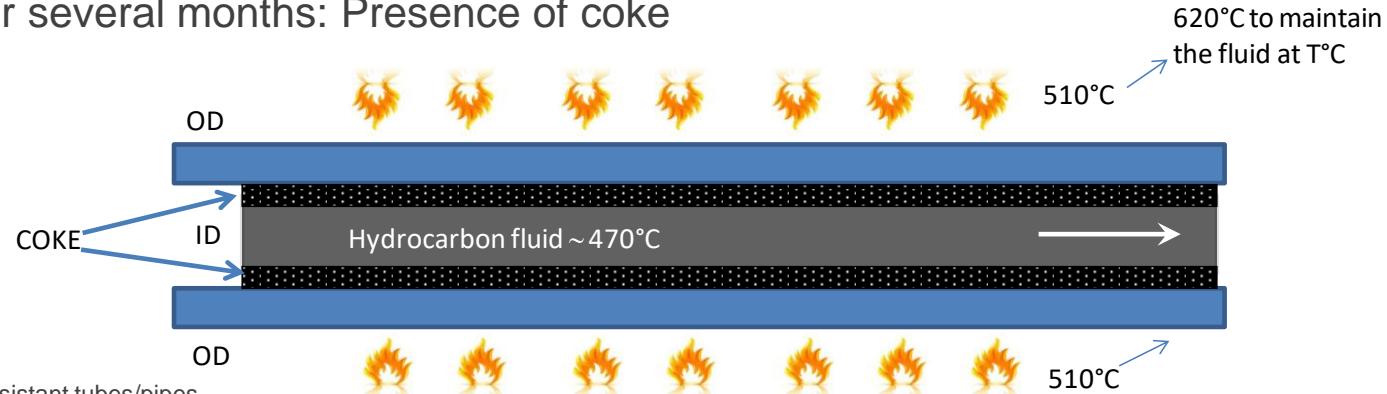
P9MOD: COKE RESISTANT TUBES/PIPES

► Reasons of development of this new material?

- Explanation



- After several months: Presence of coke



P9MOD: COKE RESISTANT TUBES/PIPES

- ▶ Reasons of development of this new material?

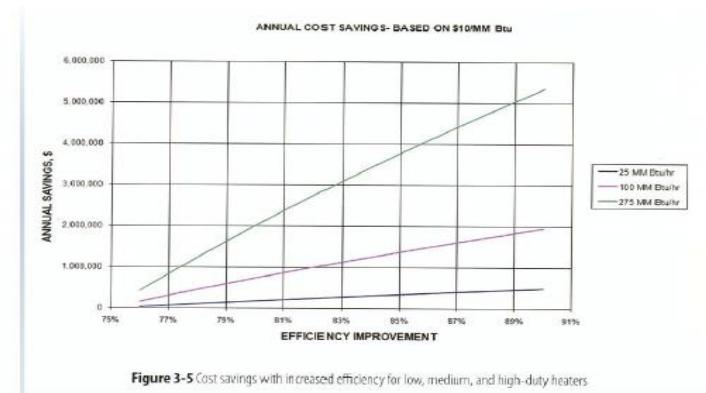
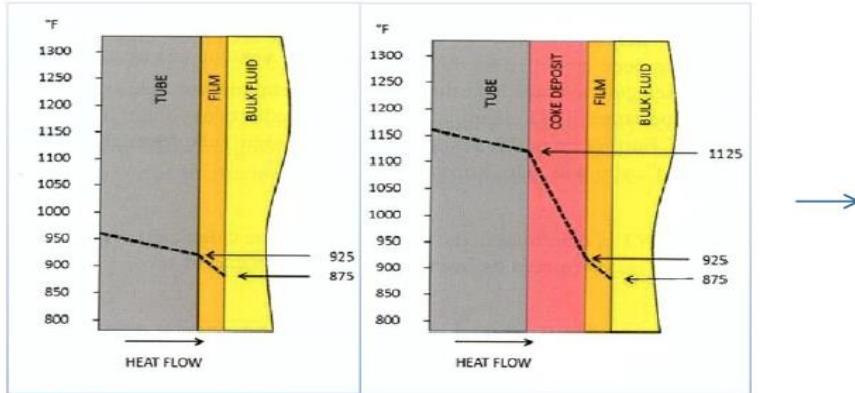


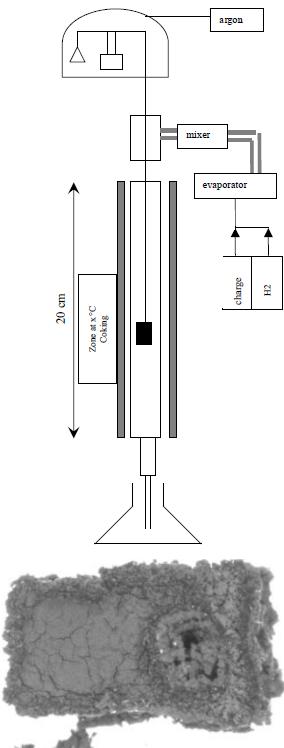
Figure 3-5 Cost savings with increased efficiency for low, medium, and high-duty heaters

Source: R. Newham, Born Heaters/OnQuest, 2012

Coking leads to energy inefficiency and to costly necessary decoking operations:

- Energy inefficiency (see above)
- Decoking Operations (source British Petroleum Gelsenkirchen July 2013):
 - Visbreaker - 100 k€ - 150 k€ per day of planned shutdown x ~ 10-14 days per year
 - Delayed Coking Unit - 400 k€ per day

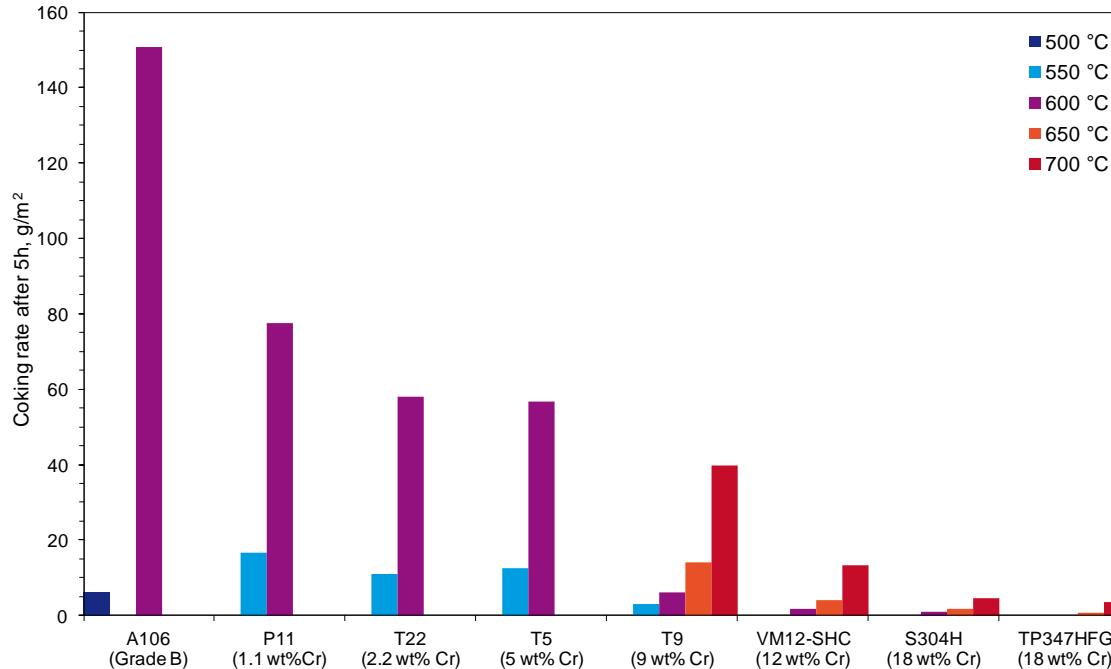
► Reasons of development of this new material? - **Benchmarking**



- Coking tests were done at the IFPEN (French Institute of Petroleum):
 - » Naphtha + Hydrogen environment → coking environment ($H_2/HC > 4$)
 - » Continuous recording of the mass gain:
 - Mass gain = coking deposit
 - Micrographic inspection
 - » Test duration: up to 18 h (maximal duration capable with this equipment)
 - » Tested temperature: 650°C and 700°C
 - Below no material screening is possible as the coking is highly reduced

**Ranking of our materials and other candidates
in order to determine an optimized chemical
composition**

- ▶ Reasons of development of this new material? - **Benchmark of steel grades**



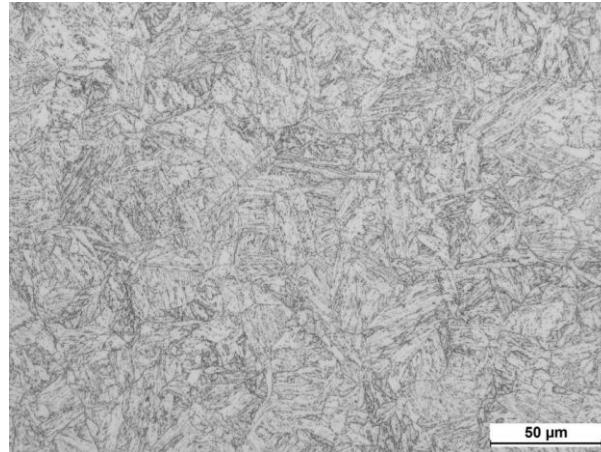
POSITIVE EFFECT IS ACHIEVED BY INCREASING Cr-ALLOYING CONTENT

- ▶ The aim is to develop material based on the Grade P9, modified to get improved anti-coking performances:
 - The following specifications have to be considered:
 - » Mechanical properties (toughness and tensile properties) in accordance with the P9 grade
 - » Martensitic microstructure with no delta ferrite to avoid issues during piercing
 - » Provided anti-coking performance
 - » Similar heat treatment as Grade P9
 - ThermoCalc (®) and Schaeffler diagram:
 - » On Schaeffler diagram → close as possible to the martensitic domain
 - » On ThermoCalc (®) simulations, different points were controlled,
 - austenite transformation temperature
 - Phases formed during the heat treatment (nitrides, carbo-nitrides and/or carbides)
 - Tempering conditions similar to Grade P9

P9Mod: coke resistant tubes/pipes

► Qualification tests results - **Chemical composition (in wt%)**

		Fe	C	Si	Mn	P	S	Cu	Cr	Mo	Ni	Al	N
P9 mod	min.		0.06	1	0.3	-	-	0.45	7.9	0.76	0.43	0.005	0.01
	max.		0.17	3	0.9	0.03	0.025	2.1	10.1	1.15	2.77	0.025	0.05

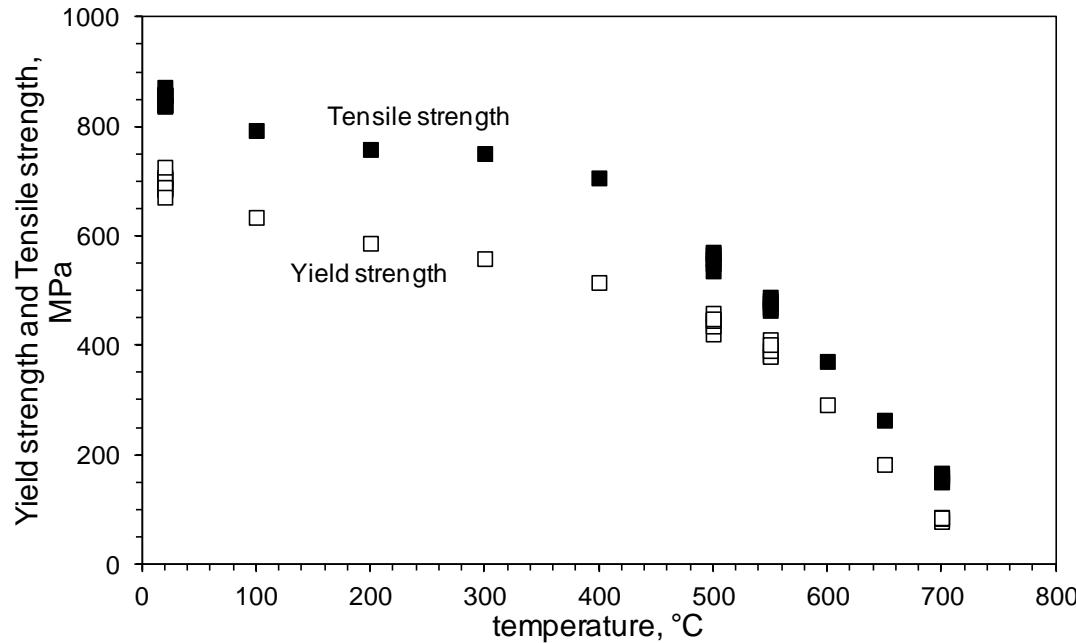


P9MOD MATERIAL IS A FULLY FERRITIC-MARTENSITIC STEEL

P9Mod: coke resistant tubes/pipes

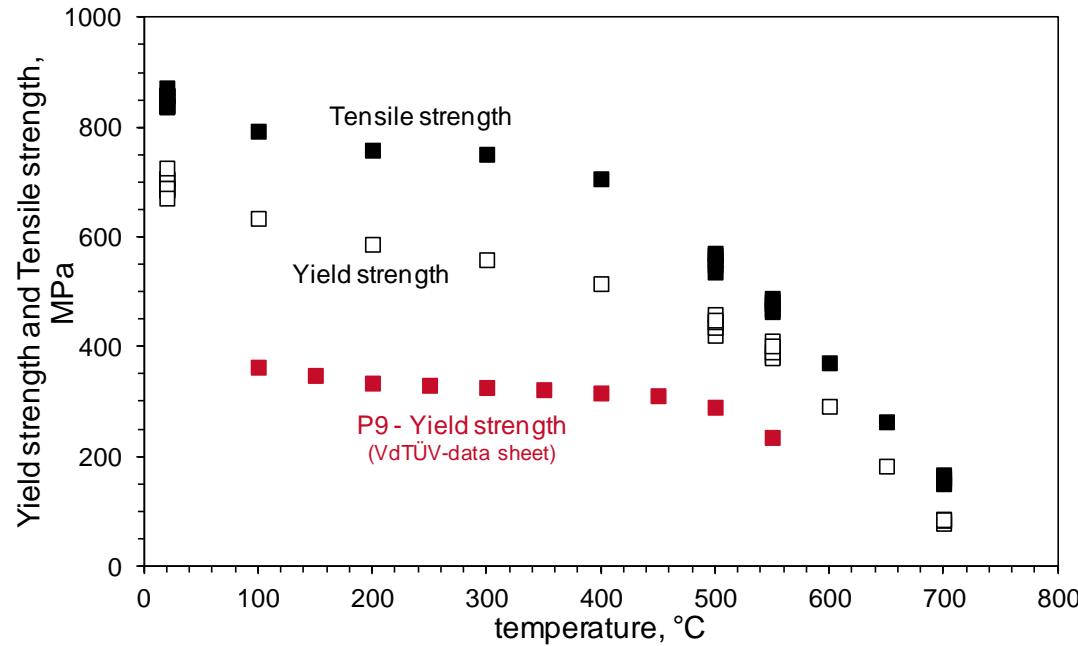
- ▶ What are the main modifications of the new chemistry vs. Grade P9?
 - Silicon
 - » together with Chromium drastically reduce the coking rate
 - Nickel
 - » is used to avoid delta ferrite (gamma-phase producing) formation and to improve toughness values
 - Copper
 - » together with Silicon also reduces the coking rate
 - If a weak zone appears on the oxide layer (cracks) then the catalytic effect of Iron will be reduced by the presence of Cu

► Qualification tests results - **Hot tensile tests**



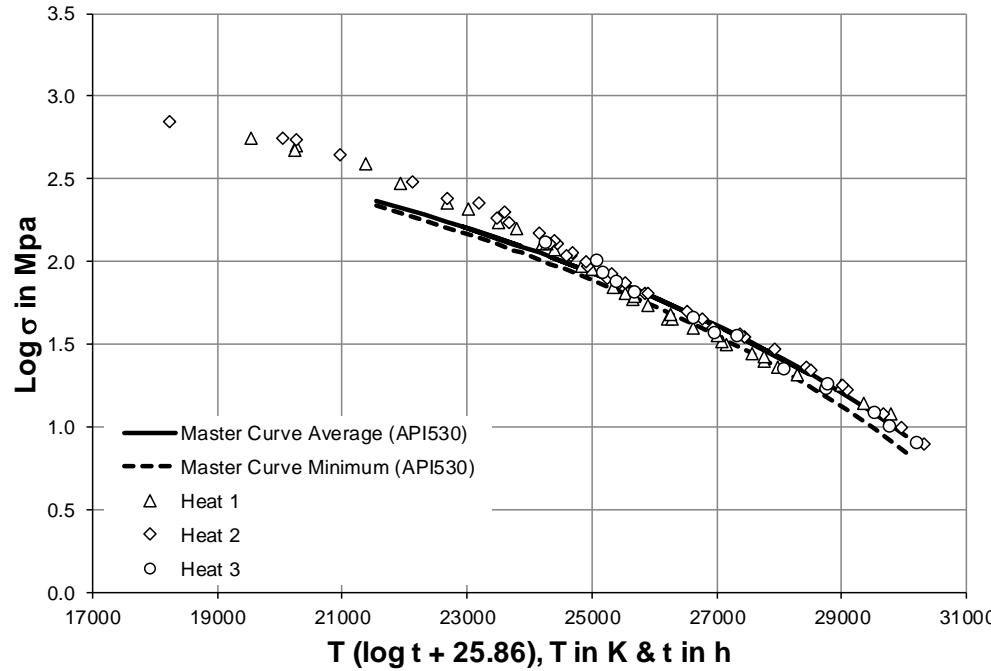
P9MOD STEEL EXHIBITS INCREASED TENSILE PROPERTIES

► Qualification tests results - **Hot tensile tests**



P9MOD STEEL EXHIBITS INCREASED TENSILE PROPERTIES

► Qualification tests results - Creep performance



CREEP STRENGTH COMPARABLE TO GRADE 9 PERFORMANCE

P9Mod: coke resistant tubes/pipes



Weight reduction: P9Mod vs. P9

114,3 x 8,56mm
in P9

114,3 x 4,21 mm
in P9Mod

Operational pressure calculated at 70% of material SMYS:

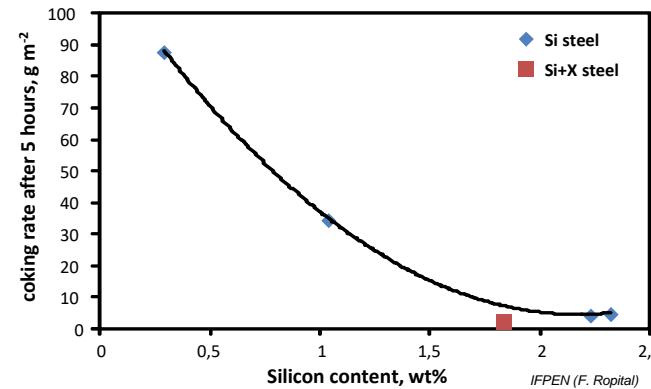
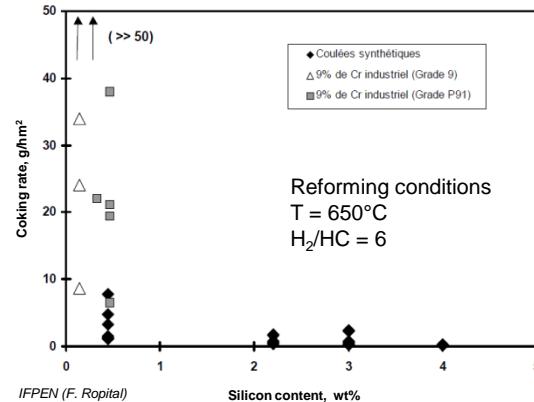
$$P_{op} = 2 * 0.7 * \text{SMYS} * \left(\frac{WT}{OD} \right) \longrightarrow P_{op} = 2 * 0.7 * \underbrace{\alpha * \text{SMYS}}_{\substack{\text{WT reduction with same factor} \\ \text{Grade increase}}} * \frac{\overbrace{WT}^{\alpha}}{\alpha} * \frac{1}{OD}$$

Gain of weight on P9 to P9Mod:

From P9	To P9	To P9Mod
Wall thickness reduction α by increasing grade		
Reduction α	0	-50,8%
WT 8,56mm	8,56mm	4,21 mm
Application with pipe OD = 114,3 mm		
Linear weight of a 10m pipe (kg)	223kgs	114kgs

Weight savings on 10m pipe :109 kgs
between 114,3x8,56mm in P9 to 114,3 x 4,21mm in P9Mod
for equivalent properties dedicated for high pressure piping system
(hot rolling mill's capabilities have to be considered)

► Qualification tests results - Corrosion tests



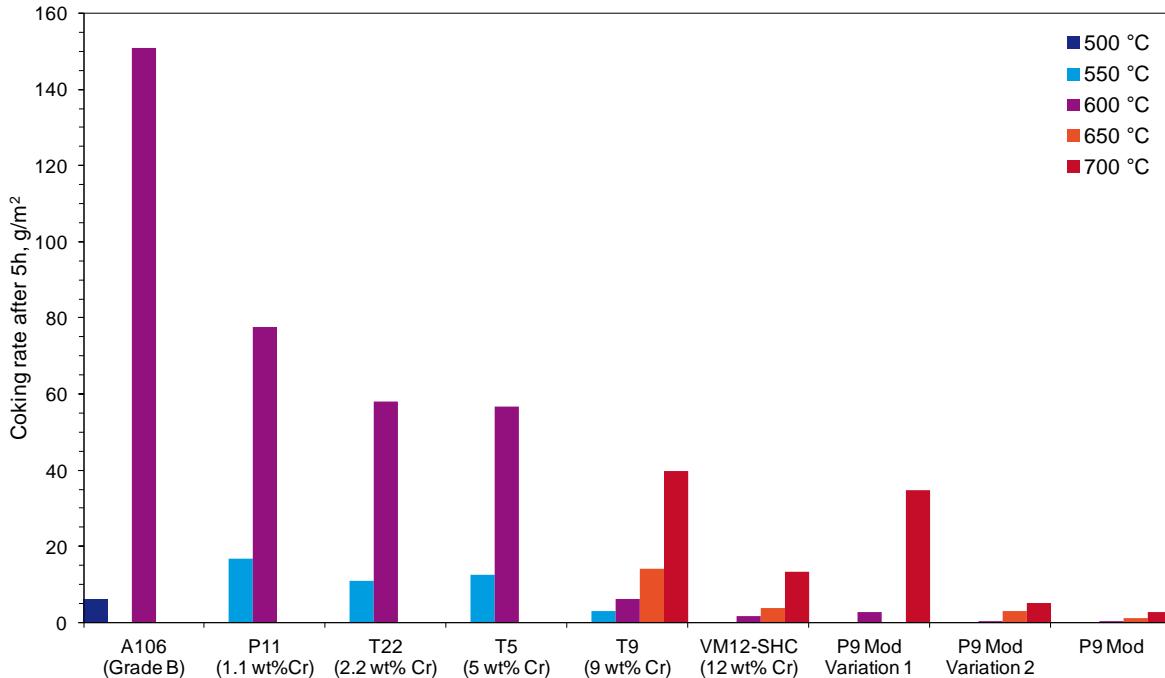
Material	600°C	650°C	700°C
	Coking level (5h) (g/m^2)	Coking level (5h) (g/m^2)	Coking level (5h) (g/m^2)
P/T9	6.2	14.1	39.7
P9Mod	0.4	1.2	2.8

* Laboratory test results: thermogravimetry is used by IFPEN to follow the coking deposit

DELAY COKING DEPOSIT PERFORMANCE IS MORE THAN x10

P9Mod: coke resistant tubes/pipes

► Laboratory test results - Thermogravimetric data



Naphtha IFPEN 7939	
Paraffin	48.5 %
Naphthalene	36 %
Benzene	0.1 %
Toluene	4.3 %
Aromatics	11.1 %
Density (g/cm ³)	0.754
Molecular weight (g/mol)	112.1
KUOP	11.9

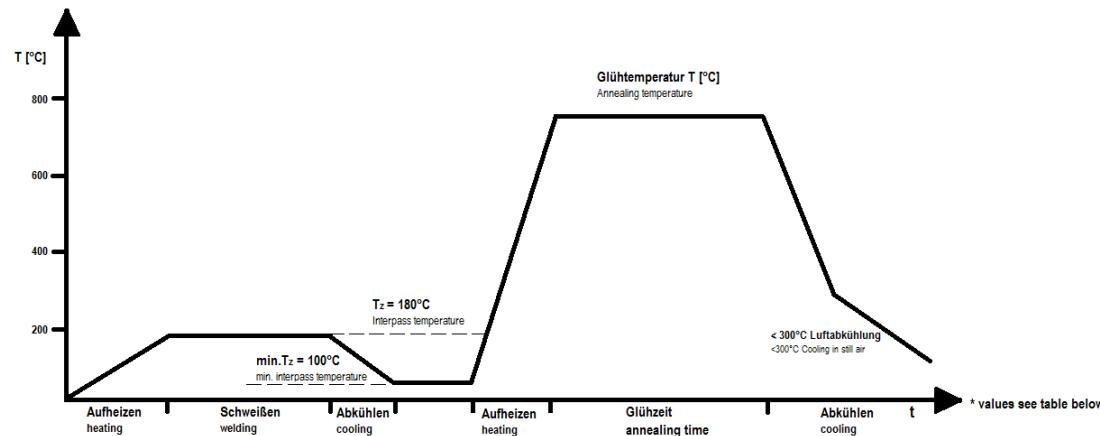
P9MOD EXHIBITS VERY LOW COKING RATES

P9Mod: coke resistant tubes/pipes

► Qualification tests results - Weldability

- Internal trials in Vallourec Research Center in Germany were performed with industrial equipments
 - P9mod shows excellent weldability
 - WPS is available

vorläufige Schweißanweisung		Bf Gütekennzeichen Schweißanweisung	
Antragsteller:		Bf Gütekennzeichen Schweißanweisung	
Auftraggeber:	Bf Gütekennzeichen		
Antrags-Nr.:			
Antrags-Name:			
Antragsteller-Nr.:			
Antragsteller-Name:			
Name:	EN ISO 9617	Weisungszeit:	Ausgabe:
	00-00-0001		Revision:
			Mischwert:
		VW-02	Paraphrasiert:
Werkstoffart:	PG mod		
Paraffinqualität:	A2		
Paraffinproduktionsdatum:	05.06.		
Paraffinherstellungszeit:	114 mm		
Paraffinmessungen:	-		
Paraffinmaße:	-		
Paraffinlängen:	0,5 mm		
Ansatz der Schweißart:	1		
Wärmeleitfähigkeit:	0,15 W/mK		
Vorwärmtemperatur:	200°C - 350°C		
Kontrolltemperatur:	W10		
Widerstandswert:	Widerstand CRW - 15		
Stahlbeschreibung:	S235 J2G3 - H		
Stahlgruppe:	S235		
Stahlzähligkeit:	ISO 14175 - II (A)		
Stahlspannung:	100 MPa		
Stahltemperatur:	-40°C bis +400°C		
Zeichner/Zeichnerin:	Herrn		
Zeichner/Zeichnerin:	Dipl.-Ing. Peter Preißel		
Zeichner/Zeichnerin:	00102019		
Prüfung:	Empfohlen		



DELAY COKING DEPOSIT PERFORMANCE IS MORE THAN x10

P9Mod: coke resistant tubes/pipes

► Qualification tests results - **Bendability**



- Industrial feasibility of elbows/fittings ($90^\circ, 180^\circ$) has been demonstrated:
 - Mechanical properties and microstructure in accordance with base metal after heat treatment

P9Mod: coke resistant tubes/pipes



► Standardization

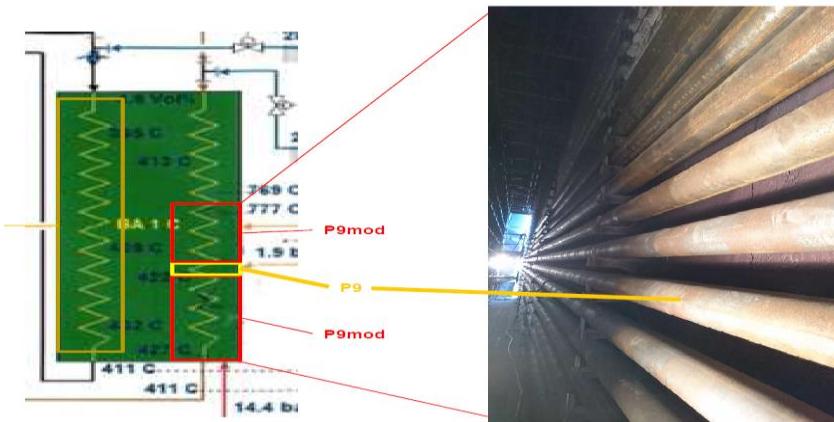
- Product Patent pending
- VdTÜV data sheet (WB 588) obtained end of 2018
 - » 10 000h creep testing already performed
 - » Mechanical testing achieved successfully
 - » under TUV inspection on industrial tubes
 - » Welding testing in progress under TUV inspection
- ASME Code Case
 - » Program in progress with creep testing
 - » Creep tests: 30,000 h on 3 different industrial heats
 - » Data package (mechanical testing, weldability, hot tensile testing, etc....)
 - » Main goal is to implement our new material in API 530

VdTÜV-Werkstoffplatt				WB Entwurf 588										
		Wärmebehandelter Stahl Rohr Nahtloses Rohr	Entwurf 588	2018-11-21										
<p>Die VdTÜV-Werkstoffpläte werden in Zusammenarbeit mit den Werkstoffherstellern erstellt und sind eine Kurzfassung des technischen Dokumentes des Betriebsherrn einer TÜV-Rheinland AG. Soweit der Technische Regeln oder Standardvorschriften Anwendung finden, ist die VdTUV-Werkstoffplatt ein Dokument nach DIN EN 1021-6 (siehe Absatz 7). Die VdTUV-Werkstoffplatt ist von den Festlegungen der nachstehenden Abschnitte und Verweisangaben zwischen Werksteller, Besteller/Werksverwalter und dem Betriebsherrn zu trennen und Erweiterungen oder ergänzende Regelungen dürfen nicht vorgenommen werden.</p> <p>Diese Platte gilt für nahtlose Rohre.</p> <p>Mitgliedige Unterlagen: DIN EN 1021-6-Z Nachweise Stahlhersteller für Rohrherstellung – Technische Dokumentationen, die für Rohre aus ungesteigerten legierten Stählen mit festgelegten Eigenschaften bei erhöhten Temperaturen</p> <p>Deutschland</p> <p>1. Hersteller/Werk VAD Vallourec Deutschland GmbH Werk Mühlen, D-Selva</p> <p>2. Markenbezeichnung und Stempelzeichen PMod</p> <p>3. Erzeugnismix, Abmessung und Lieferzustand</p> <table border="1"><tr><td>Herdsteller</td><td>Werk</td><td>Erzeugnisform</td><td>Wanddicke</td><td>Lieferzustand</td></tr><tr><td>VAD</td><td>Mühlen St. Selva</td><td>Rohr</td><td>max. 20 mm max. 20 mm</td><td>vergütet</td></tr></table> <p>4. Erschmelzen Elektrolytischschmelzen (ES) mit Vakuum Umgang oder vergleichbarer Nachbehandlung</p> <p>5. Desoxidieren Besonders wichtig</p> <p>6. Weitere Herstellungseigenschaften verriegelt</p> <p>7. Technische Überwachungsorganisation, die Mitglied im VdTUV ist</p> <p>Zusammengestellt nach Angaben des TÜV Rheinland</p> <p>Die VdTUV-Werkstoffplatt wird unterschrieben, geschult ist die Verarbeitung, die Herstellung und die Herstellergüteprüfung von Rohren aus ungesteigerten legierten Stählen mit festgelegten Eigenschaften bei erhöhten Temperaturen. Die VdTUV-Werkstoffplatt ist eine Kurzfassung des technischen Dokumentes des Betriebsherrn einer TÜV-Rheinland AG. Soweit der Technische Regeln oder Standardvorschriften Anwendung finden, ist die VdTUV-Werkstoffplatt ein Dokument nach DIN EN 1021-6 (siehe Absatz 7). Die VdTUV-Werkstoffplatt ist von den Festlegungen der nachstehenden Abschnitte und Verweisangaben zwischen Werksteller, Besteller/Werksverwalter und dem Betriebsherrn zu trennen und Erweiterungen oder ergänzende Regelungen dürfen nicht vorgenommen werden.</p> <p>Herausgeber: Werkstatt der TÜV A. G. Gesamt und Inhaltlich TÜV Rheinland AG verantwortlich. Urheberrecht: TÜV Rheinland Group</p>					Herdsteller	Werk	Erzeugnisform	Wanddicke	Lieferzustand	VAD	Mühlen St. Selva	Rohr	max. 20 mm max. 20 mm	vergütet
Herdsteller	Werk	Erzeugnisform	Wanddicke	Lieferzustand										
VAD	Mühlen St. Selva	Rohr	max. 20 mm max. 20 mm	vergütet										

P9Mod: coke resistant tubes/pipes

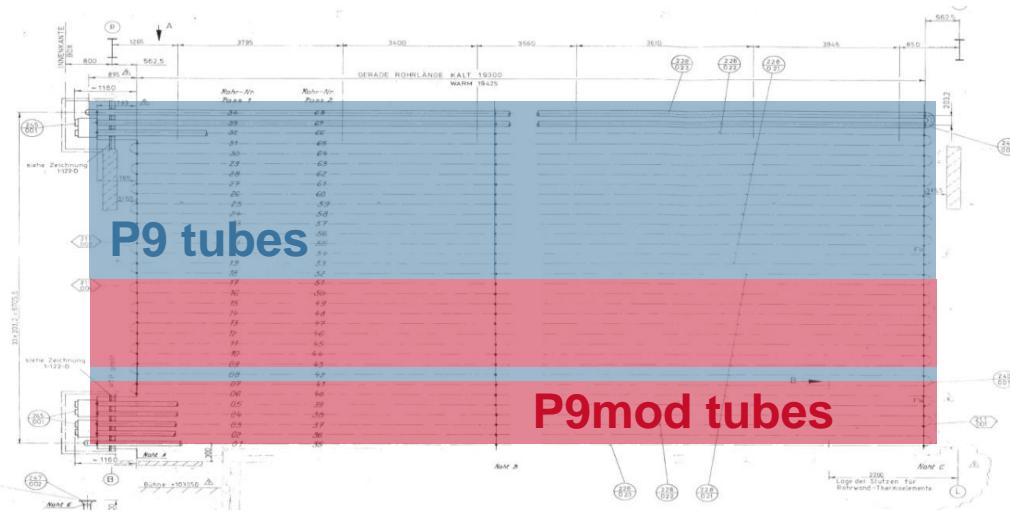
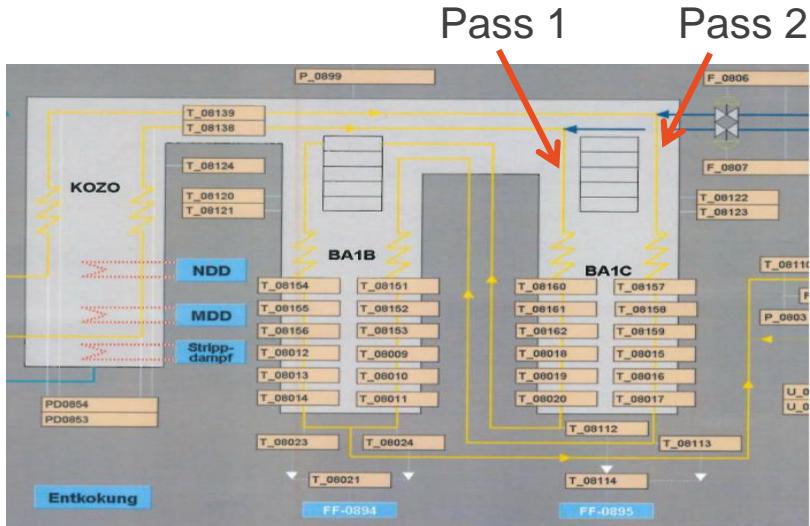
► Field testing

- In progress within one visbreaker in Europe under SMA (Single Material Appraisal) approval:
- Tubes have been installed one year ago and samples have been cut off for investigation



P9Mod: coke resistant tubes/pipes

- ▶ Tubes installed in the Visbreaker furnace



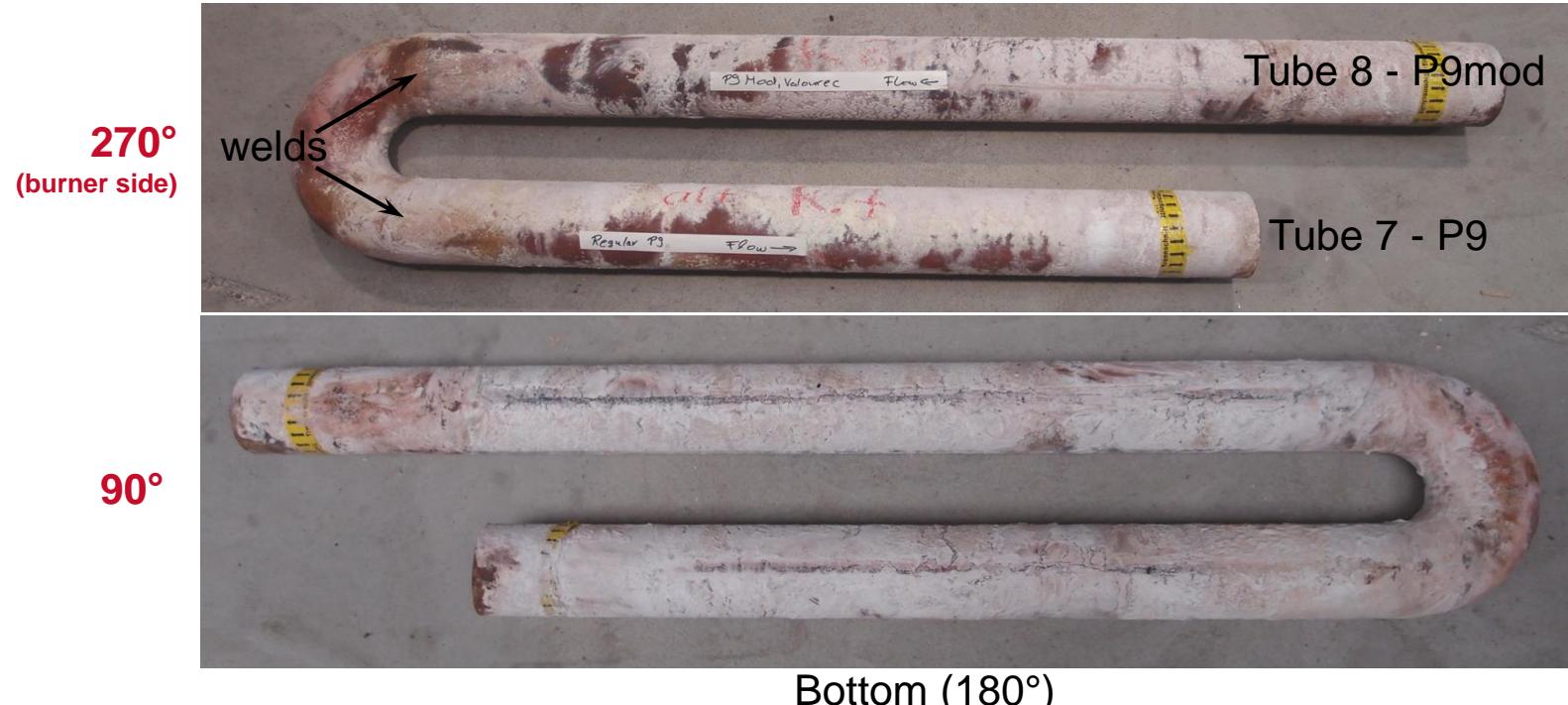
Pass 1: 100% with P9 tubes installed

Pass 2: mix of P9 and P9mod tubes (16 P9mod tubes + 1 P9 tube)

P9Mod: coke resistant tubes/pipes

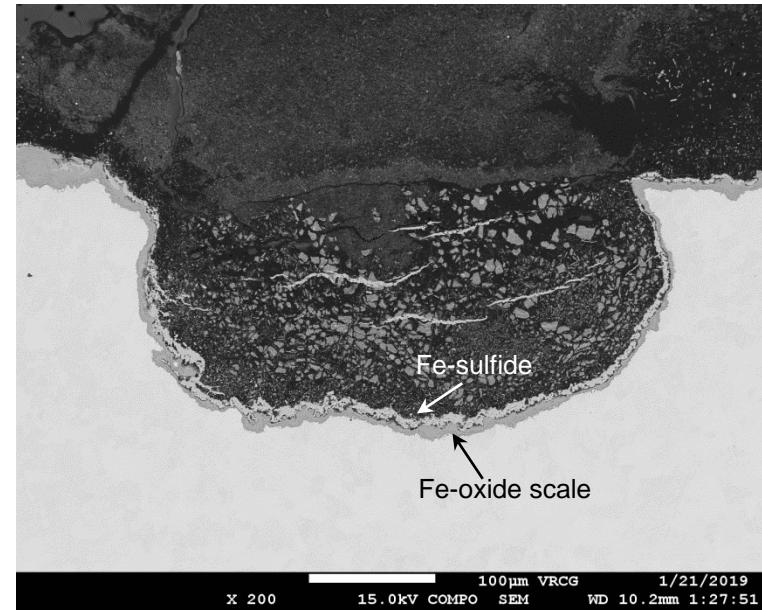
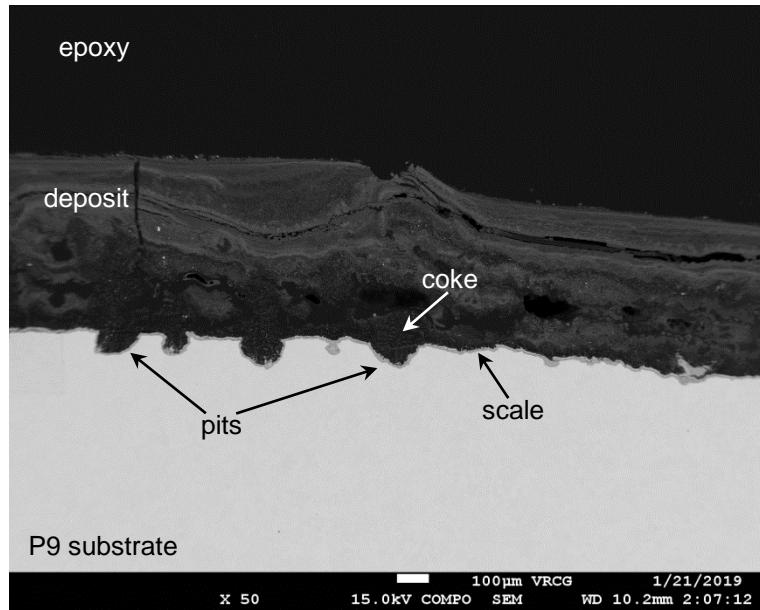
- Field testing in Visbreaker - **After 1 year operation**

Top (0°)



P9Mod: coke resistant tubes/pipes

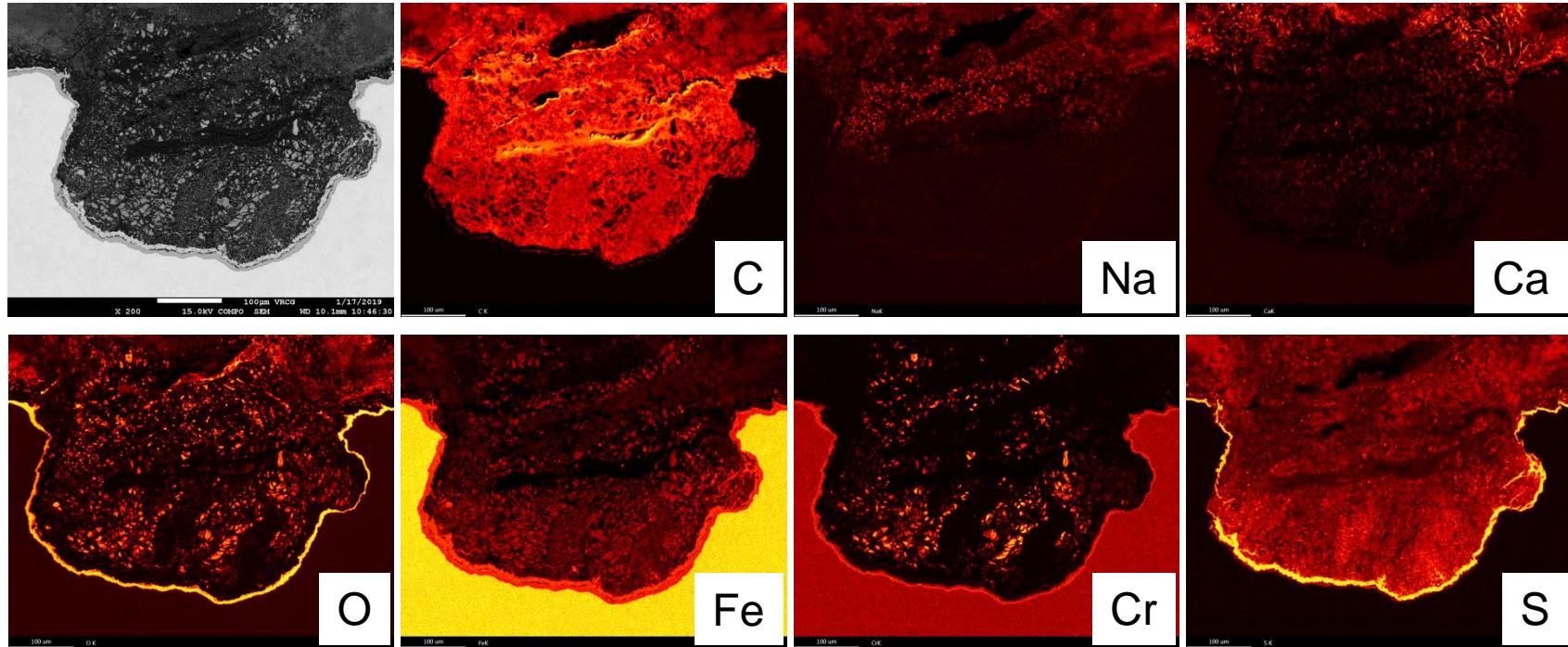
- Field testing in Visbreaker - **P9 steel after 1 year operation**



P9 STEEL TENDS TO FORM LARGE PITTINGS

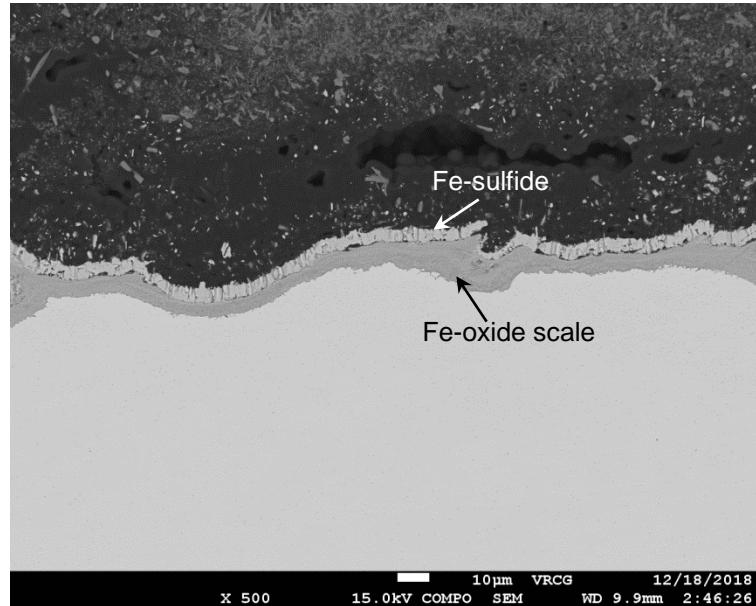
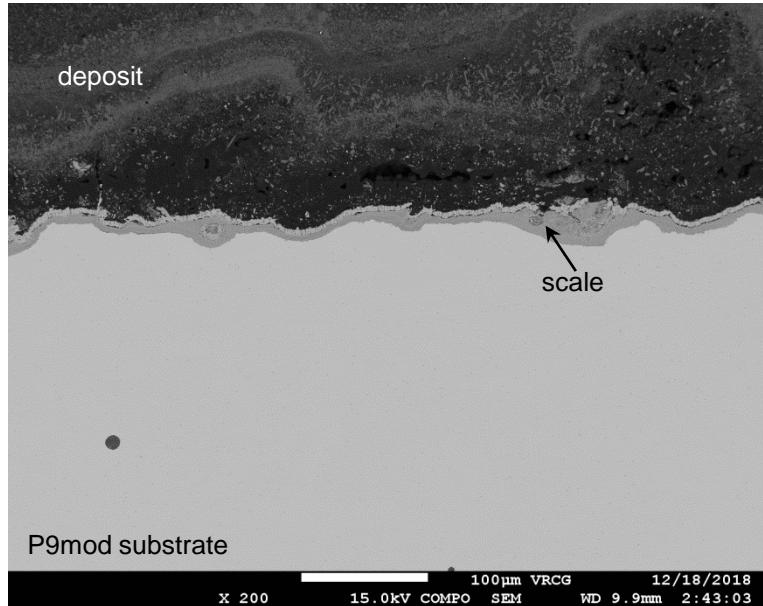
P9Mod: coke resistant tubes/pipes

- Field testing in Visbreaker - **P9 steel after 1 year operation**



P9Mod: coke resistant tubes/pipes

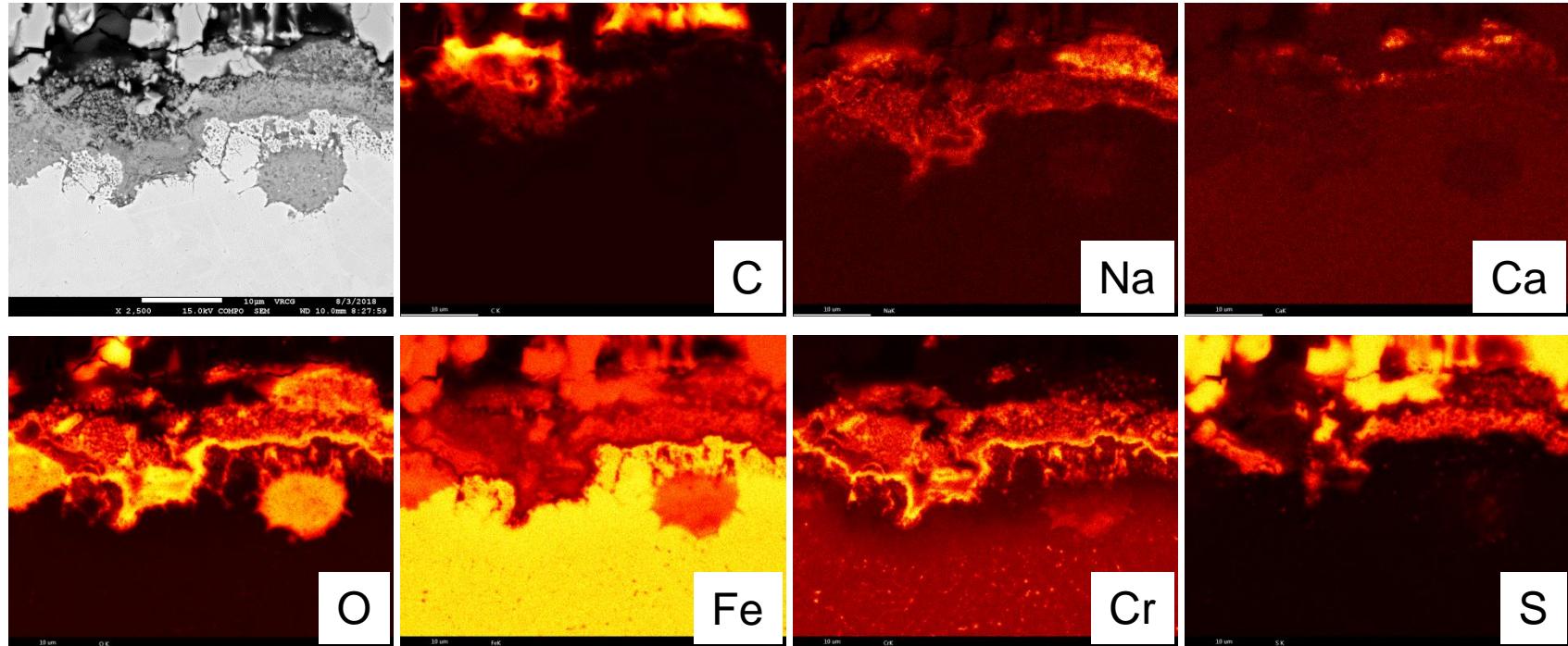
- Field testing in Visbreaker - **P9mod steel after 1 year operation**



P9MOD STEEL NO PRESENCE OF PITTINGS WAS OBSERVED

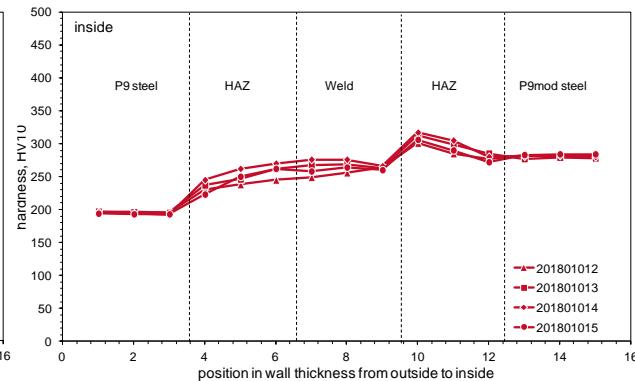
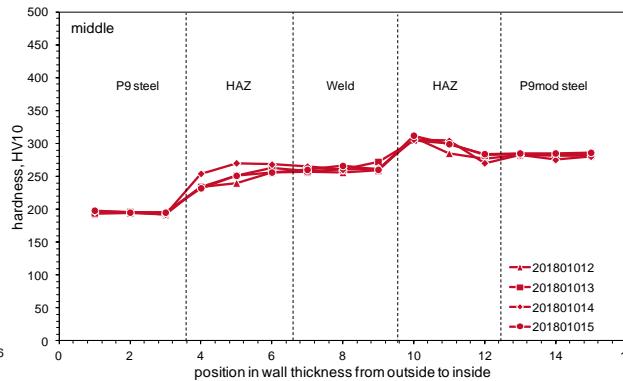
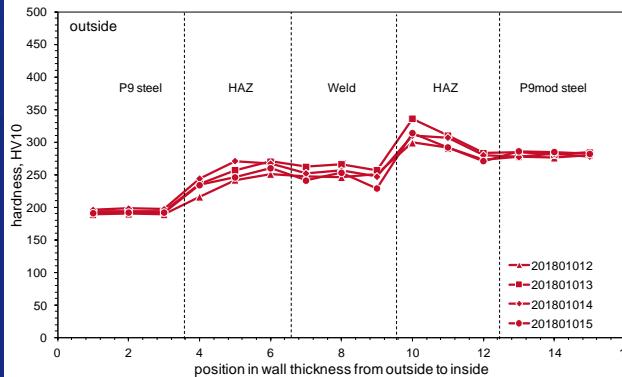
P9Mod: coke resistant tubes/pipes

- Field testing in Visbreaker - **P9mod steel after 1 year operation**

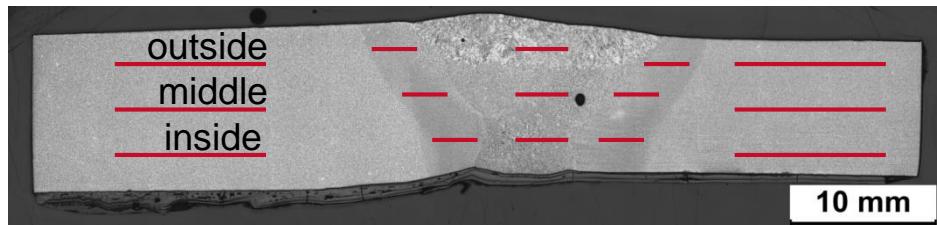


P9Mod: coke resistant tubes/pipes

► Visbreaker - Weldability: after 1 year operation



P9 HAZ weld HAZ P9mod



Conclusions

- Decrease the fuel consumption by increasing the furnace thermal efficiency.
- Increase the reaction volumes/unit capacity which is normally declining due to tube obstruction
- Decrease the tube replacement by reducing wear due to regular pigging operations
- Decrease maintenance costs due to coke resistance effect: decrease frequency of maintenance stoppage
- Product can be used under SMA/PMA approval with specific testing according to standard used.
- Field testing very promising according to feedback of user
- Standardization: VdTÜV data sheet obtained end of 2018. ASME code Case process in progress
- Highest mechanical properties as for P9: design issues (wall thickness reduction, better heat transfer), wearing resistance (pigging, maintenance)
- Field testing under higher temperature has to be done in order to check the efficiency of P9Mod: coil visbreaker instead of soaker visbreaker

- ▶ Back up



Topsides / FPSO

(Floating, Production, Storage and Offloading)

- High pressure
- High salinity water
- Corrosive fluids (H_2S)
- Reinjection of CO_2 (low temperature)



Oil Sands

- In situ recovery (hot water)
- Upgraders (H_2S)
- Dilbit (abrasion)



Onshore Line Pipe

- Stringent environments
- Bending
- Welding



EOR / Sour Gas Injection

- Corrosive fluids
- High pressure (up to 500 bar)
- Low temperature (depressurization)
- Welding

process

linepipe



LNG trains / FLNG

(Liquified Natural Gas / Floating LNG)

- Low temperature solutions
- Weight / volume optimization



Fired Heaters

- High temperature
- Coking
- Corrosive fluids (H_2S)



Refineries

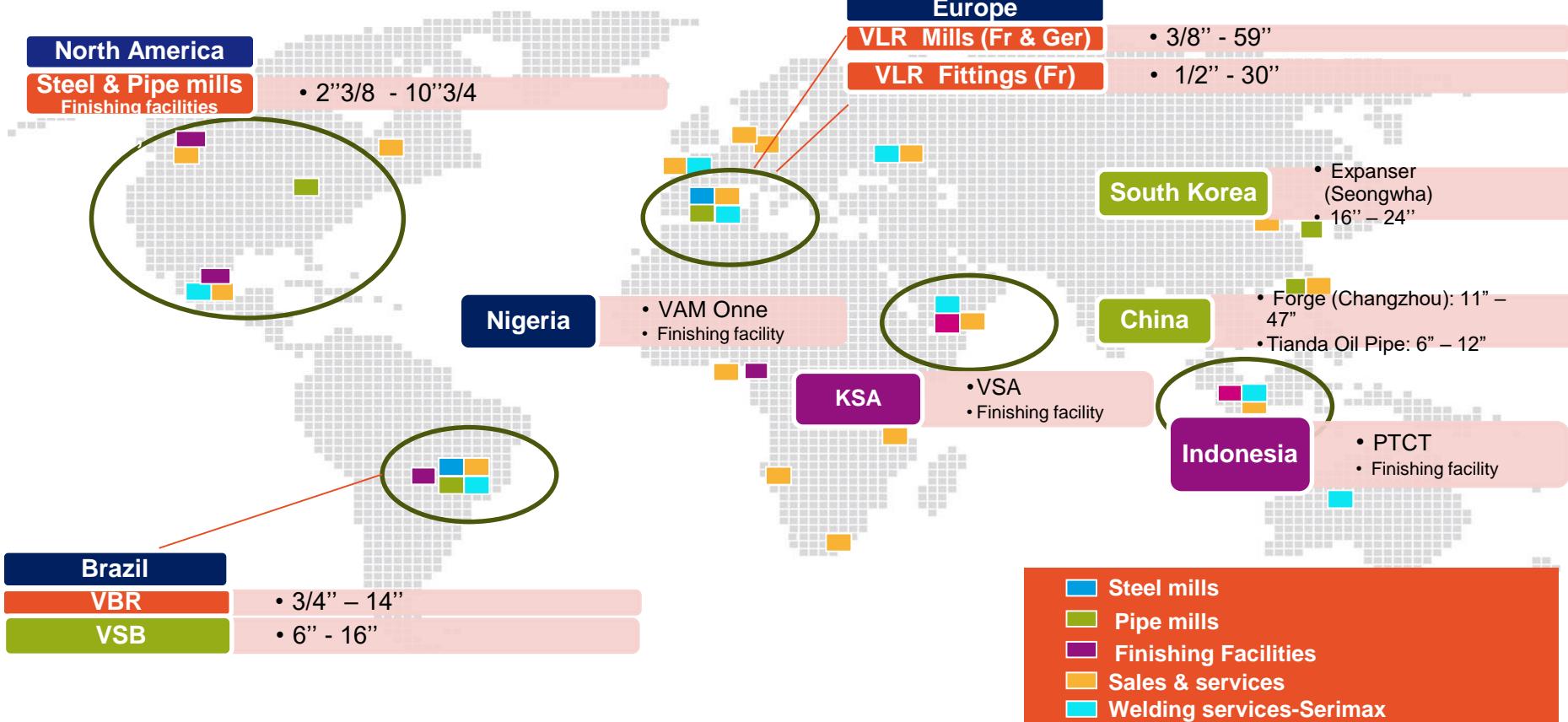
- High pressure
- High temperature
- Corrosive fluids (H_2S , CO_2)
- Wide range of viscosity



Petrochemicals

- High pressure
- High temperature
- Corrosive fluids (H_2S , CO_2)

Our footprint Global & Local – Close to your needs !



VALLOUREC: A PARTNER OF CHOICE



Here are some (but not all) of our partners ...

Operators / EPCs



Distribution Partners



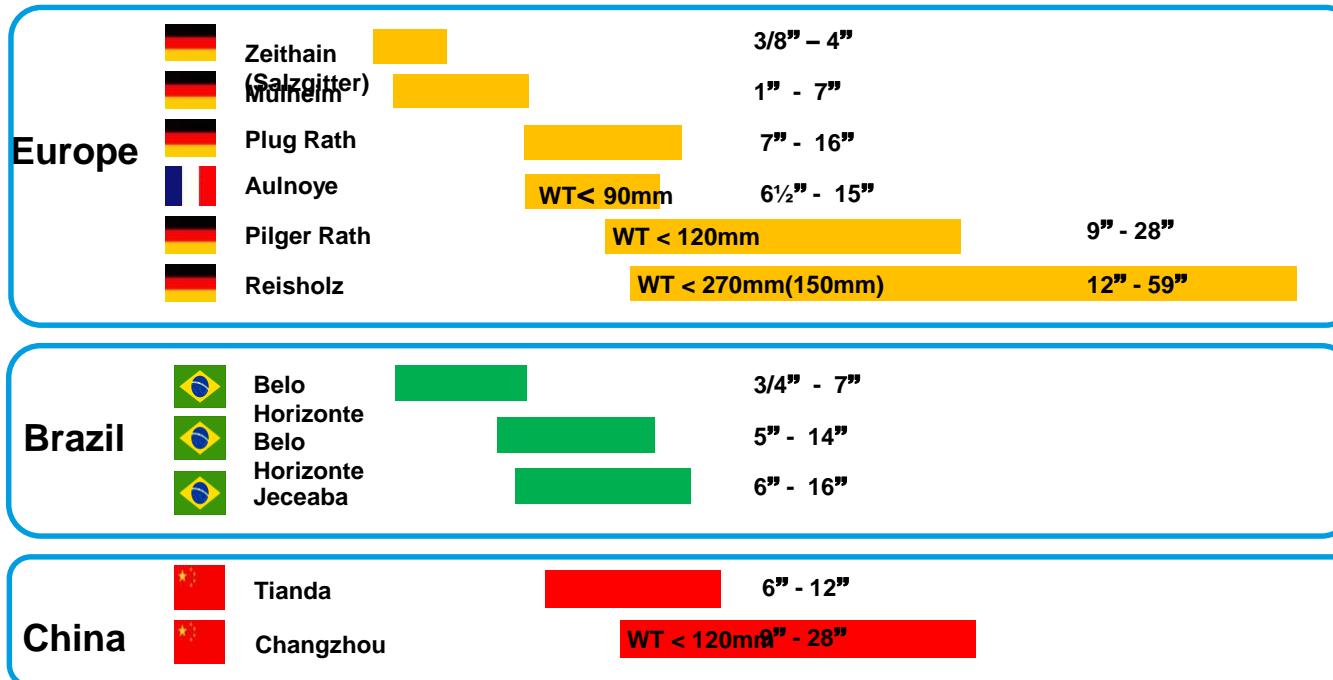
Customers in SA



Services



A FULL RANGE OFFER OF GRADES AND SIZES



Brazil and China : two competitive routes for international markets